

Mercury Control with Calcium-Based Sorbents and Oxidizing Agents

Quarterly Report

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Prepared by

Thomas K. Gale

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Southern Research Institute

2000 Ninth Avenue South

P. O. Box 55305

Birmingham, AL 35255-5305

Prepared for

Barbara Carney

National Energy Technology Laboratory

United States Department of Energy

626 Cochrans Mill Road

Pittsburgh, PA 15236-0940

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Abstract

Some time was spent this quarter on preparing for new project tasks, following the results obtained from the ARCADIS benchscale tests. However, pilot-scale tests were also delayed by mercury monitor problems. A list containing many typical monitor failings is included in the report. However, the unique *spike and recovery* system used by SRI in this work was essential to identifying many of these problems. Data reported by individuals or entities, without such Q/A ability and procedures, should be regarded as highly suspect. This *spike and recovery* system was also essential to finding solutions to monitor problems and in correcting data where possible.

Unfortunately, several severe problems with the PS Analytical mercury monitor prevented extensive testing from being performed this quarter. Nevertheless, some meaningful results have been obtained.

The ability was demonstrated to test multiple fuels in the CRF with only several (~5) hours transition, without interference dominating from previously deposited ash. The value and importance of the *spike and recovery* system to Hg-monitoring was illustrated, allowing low uncertainty results to be obtained for mercury speciation, while firing PRB coal in the CRF.

It was also shown that HCl, produced by injecting Cl₂ through the burner, conditioned PRB ash downstream, making it effective at removing oxidized mercury, ahead of and possibly in a mass-train filter. Chlorine gas (Cl₂—injected above the air heater (1064 °F)) was ineffective at conditioning the ash for mercury sorption, even though it was effective at oxidizing the elemental mercury to form HgCl₂.

Finally, kaolinite (Al₂O₃·2SiO₂·aH₂O), a very effective sorbent for capturing semi-volatile metals (Pb, Cd, and Na), was shown to be ineffective at capturing mercury at either high, low, or intermediate temperatures.

Future tests are planned for the upcoming year to investigate the mechanisms of Hg-speciation and capture as a function of ash composition, including testing of coal-ash blends and injection of high-iron flyash into the baghouse, while burning PRB coal.

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Introduction

The results from three separate investigations performed this quarter are presented in this quarterly report, (1) PRB speciation in the CRF, (2) a kaolinite sorbent test, and (3) chlorine injection effects on mercury speciation. The data obtained was in collaboration with a mercury speciation project funded by EPRI, TVA, Southern Company, and EPA (funds from this other project helped pay for some of the testing). Hence, the cost to DOE for this work was less. Much of the effort spent this quarter has been in mercury monitor development. The PS Analytic Hg-monitor possesses a high lack of robustness. Consequently, much effort has been spent fixing the monitor system and customizing it for more robust operation. The following is a list of problems that SRI has experienced with the PSA monitor:

- 1) Severe interferences caused by moisture condensation in the transfer line between the gas conditioning systems and the Hg-monitor.
- 2) Impinger reagent contamination.
- 3) Fluctuating optics parameters in the Sir Galahad Hg-monitor.
- 4) Fluctuation of the internal mass flow controller.
- 5) Gold-trap contamination.
- 6) High sensitivity to line voltage.
- 7) A general lack of robustness of the Sir Galahad monitor, switching box, mass flow meters, impingers, heaters, pumps, condensing unit, and moisture sensor.
- 8) Impinger chemistry incompatibility with various flue-gas compositions.
- 9) Precipitation of tin oxide in the stannous chloride (total mercury) impinger.
- 10) Optics, electronics, and other systems high sensitivity to ambient temperature fluctuations.
- 11) Flyash interactions and interferences when sampling.
- 12) Acid gas, particularly chlorine, interference with Hg-measurements.
- 13) Atomic-fluorescence lamp instability and instrument drift.

Fortunately, through interactions with PS Analytical and careful development of ancillary features of an *advanced spike and recovery system*, SRI has been able to detect, diagnose, and resolve or otherwise correct for all of the problems that would otherwise yield poor data.

Experimental

The Combustion Research Facility (CRF) at Southern Research Institute (SRI) was fired at 1.0 MW thermal or about 0.35 MW electric. The design of the facility was carefully chosen to provide a close simulation of the physical processes that occur in a full-scale utility boiler. The facility, shown in Fig.1, consists of a coal crushing and milling area, a coal feeding system, a vertical refractory lined furnace, a single up-fired burner, a horizontal convective section pass with air-cooled tube banks, a series of heat exchangers, an electrostatic precipitator, a pulse jet baghouse, and a packed column scrubber.

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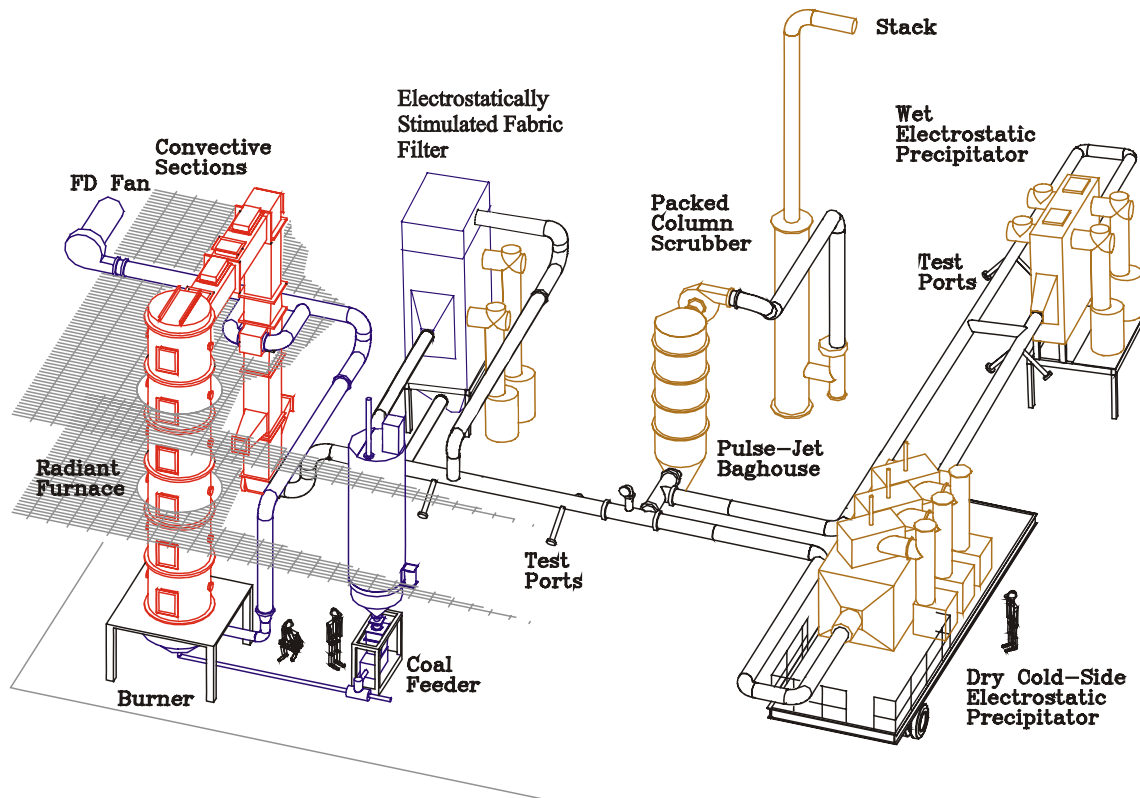


Figure 1. The Southern Company / Southern Research Institute Combustion Research Facility.

Fuel Preparation

The fuel preparation area includes an open area storage yard, covered on-site storage bins, a rotary drum coal crusher, a CE Raymond bowl mill, and pulverized coal storage. The coal mill is a refurbished and instrumented Model 352 CE-Raymond bowl mill, which has a rated capacity of 2 tons per hour. This type of mill should give representative milling simulations of the different air-swept table and roller mills normally used in power plant service.

Temperature/Time History Comparison

The temperature/time history within the Combustion Research Facility (CRF) is consistent with that of full-scale boilers, from the burner all the way through the economizer. Figure 2 shows a comparison of the CRF temperature profile with that of various Southern Company full-scale facilities.

Radiant Furnace

The furnace is a vertical, up-fired, 28-foot high cylinder, with an inner diameter of 3.5-feet (see Figure 1). This allows gas velocities of 10 to 20-feet per second and residence times of 1.3 to 2.5 seconds, depending upon the firing rate. The design furnace exit gas temperature is 2200°F.

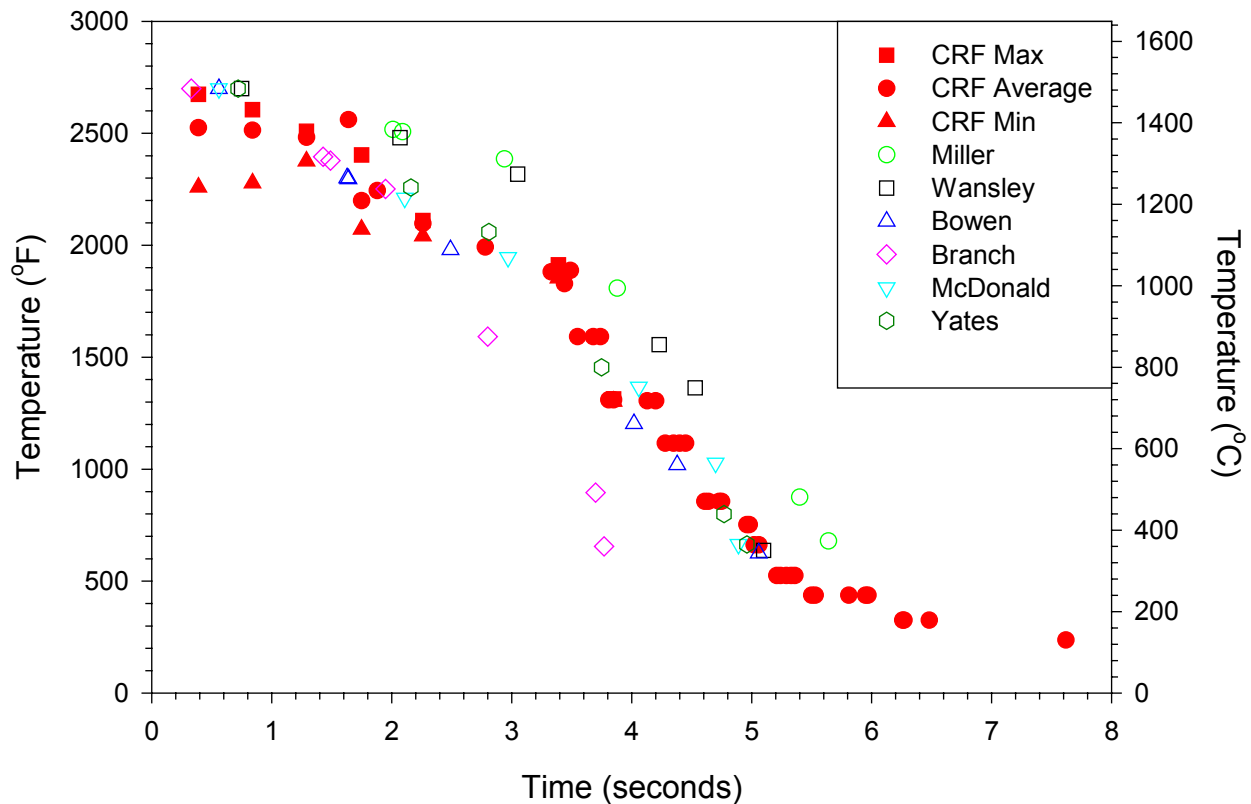


Figure 2. Combustion Research Facility (CRF) temperature/time Histories compared with those of full-scale Southern Company Services, coal-fired power plants.

Burner Assembly

The burner is mounted coaxially on the bottom of the furnace and is up-fired using natural gas, pulverized coal, any combination of the two or any other fuel that can be finely divided and transported to the pulverized coal silo. It is equipped with a flow control system for secondary air flow and a set of registers, which impart swirl to the secondary air, separate from the flow control. The secondary air and the primary air-coal mixture enter the furnace through a refractory quarl with a 25° half angle. Two clean-out ports are provided in this section, to allow bottom ash to be periodically removed from the furnace. A closed-circuit television camera with a control-room monitor allows constant monitoring of the view of the flame from the top of the furnace. A low NO_x firing system, consisting of a generic dual-register burner and an overfire air system, can be installed to simulate several combinations of low NO_x firing.

Convective Sections

The combustion gases exit the vertical furnace through a horizontal convection pass, which is designed to remove a substantial part of the heat from the flue gases. The extraction of heat is designed in order to simulate the time-temperature profile found in a utility boiler. A series of three air-cooled tube banks are installed in the convective pass, and the air cooling is used to control either the temperature profile of the flue gases or the tube metal surface temperatures for fouling/ash deposition studies. A cross-flow tubular air preheater follows the convective tube banks and is used to preheat the primary and secondary air. Finally, four air-to-flue-gas

recuperators are used to cool the flue gas down to a nominal 300°F before the flue gas enters the pollution control devices.

The convective section is 1.5 feet x 1.5 feet x 22 feet, providing gas velocities of 10 to 20 m/s (30 to 60 ft/s) and residence times of 0.4 to 0.8 seconds, again depending upon the firing rate. The design temperature range for the convective section is 1200 to 650°C (2200 to 1200°F).

Computer Data Acquisition and Control System

The facility is controlled and monitored by networked combined digital control system (DCS) and data acquisition computers, managed by Yokogawa CS-1000 system software that runs under the Windows NT operating system. This DCS performs all process control for the facility and allows complex feed-forward and calculated variable control. This computer control also performs the monitoring needed for safe operation of combustion equipment, including flame scanning and interlocks, automatic startup, and automatic shutdown of the entire facility. Process data acquisition and storage is accomplished within the Yokogawa software.

CEM System

A complete, extractive, continuous emissions monitoring (CEM) system is installed in the facility.

Pollution Control Equipment

Test equipment available for use at the Combustion Research Facility include an Electrically Stimulated Fabric Filter, a dry wall Electrostatic Precipitator, and a fluidized semi-dry / dry desulfurization system.

Mercury Measurements

An advanced and improved version of the PS Analytical mercury monitor is currently set up at the CRF, including a *spike and recovery* system. Accurate and precise mercury speciation measurements are key to a fundamental mercury speciation and capture investigation. As a result of extensive engineering, SRI can now measure mercury speciation within a maximum uncertainty of 5%, which capability is essential to the success of this project. Furthermore, an advanced *spike and recovery* system makes it possible to validate the correctness of the mercury speciation numbers measured and correct for errors that occur.

Spike and Recovery System

The *spike and recovery system*, employed for the first time on this project, is a first of its kind prototype, provided to SRI by PS Analytical, as a result of extensive discussions with various PSA personnel. The adaptation of this *spike and recovery* system to allow spiking at the tip of the APOGEE Scientific QGIS probe was performed entirely by SRI personnel. The spike of mercury is introduced into the tip of the APOGEE Scientific QGIS probe far enough downstream from the inlet to prevent losses to the duct and far enough upstream of the porous annulus to allow complete mixing before the sampled gas is pulled through the porous frit. A relatively small quantity of air is used to carry the mercury spike to the probe. Therefore, dilution is

insignificant and the general flue-gas composition is undisturbed. The main impact of the spike is simply to increase the concentration of mercury in the sampled gas. The concentration of mercury in the spike stream is generated by controlling the flow rate, pressures and temperatures of air in and through a mercury reservoir chamber. This prototype system will be improved upon, based on the information learned from this and other experiments. In addition, SRI uses a parallel Hg-source for the *spike and recovery* system, involving permeation tubes, allowing a check on the source calibration. Without spike and recovery, all Hg-monitor data reported in the literature must be regarded as highly suspect, especially with regards to Hg-speciation.

Results and Discussion

PRB Coal Analysis and Speciation Test Conditions

Powder River Basin (PRB) coal (i.e., Black Thunder) was tested in the Combustion Research Facility (CRF) at Southern Research Institute (SRI) for the first time. In addition, the first data available with *spike and recovery* validation were obtained. Mercury measurements began with a completely clean furnace, while firing on natural gas. The transition from natural gas to PRB coal-firing was observed in the mercury monitor measurements, until a stable baseline of elemental and total mercury was observed. Table 1 contains the analysis of Black Thunder Powder River Basin (PRB) coal and Table 2 contains the combustion conditions for this test.

Table 1. Black Thunder PRB Sub-bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	14.00	% Carbon	74.55	Hg ($\mu\text{g/g}$)	0.07 – 0.08
% Ash	5.92	% Hydrogen	4.78		
% Volatiles	37.57	% Nitrogen	1.03		
% Fixed C	42.70	% Sulfur	0.37	Chlorine (%)	0.0130
HV (Btu/lb)	9,969	% Oxygen	19.27		

Table 2. Combustion conditions.

Measurement	Range of Value
Overfire Air (OFA) (%)	15.0
Furnace Exit Oxygen (FEO) (%)	3.93 +/- 0.22
Coal Feed Rate (lbs/hr)	365 +/- 2.9
<u>Flue gas composition at sampling points:</u>	
Carbon Dioxide (CO ₂) (%)	14.1 +/- 0.4
Carbon Monoxide (CO) (ppm)	62 +/- 3
Oxides of Nitrogen (NO _x) (ppm)	160 +/- 8
Sulfur Dioxide (SO ₂) (ppm)	213 +/- 5
Oxygen (O ₂) (%)	6.2 +/- 0.3

Table 3. Black Thunder PRB Sub-bituminous coal ash analysis.

Parent Coal		Tube Bank		Mass Train	
% Li ₂ O	0.01	% Li ₂ O	0.02	% Li ₂ O	0.01
% Na ₂ O	1.4	% Na ₂ O	1.1	% Na ₂ O	2.4
% K ₂ O	0.50	% K ₂ O	0.65	% K ₂ O	0.61
% MgO	4.3	% MgO	3.2	% MgO	5.3
% CaO	22.0	% CaO	16.9	% CaO	27.3
% Fe ₂ O ₃	6.0	% Fe ₂ O ₃	7.3	% Fe ₂ O ₃	7.1
% Al ₂ O ₃	15.4	% Al ₂ O ₃	18.4	% Al ₂ O ₃	18.2
% SiO ₂	35.4	% SiO ₂	42.9	% SiO ₂	29.6
% TiO ₂	1.3	% TiO ₂	1.2	% TiO ₂	1.7
% P ₂ O ₅	0.70	% P ₂ O ₅	0.50	% P ₂ O ₅	1.30
% SO ₃	11.5	% SO ₃	5.1	% SO ₃	3.7
% LOI	---	% LOI	0.56	% LOI	0.23
% UBC	---	% UBC	0.14 – 0.17	% UBC	0.04 – 0.07

A temperature/time profile specifically for the PRB coal-fired conditions of this test is presented in Figure 3. Table 3 contains analysis of isokinetically sampled mass train ash during this test. A transition from PRB coal to Choctaw America coal (a low chlorine HvA bituminous coal) was also tested at the end of the PRB-only investigation. The coal analysis and conditions of this test are the same as presented in Tables 4 and 5, in the next test description of this report.

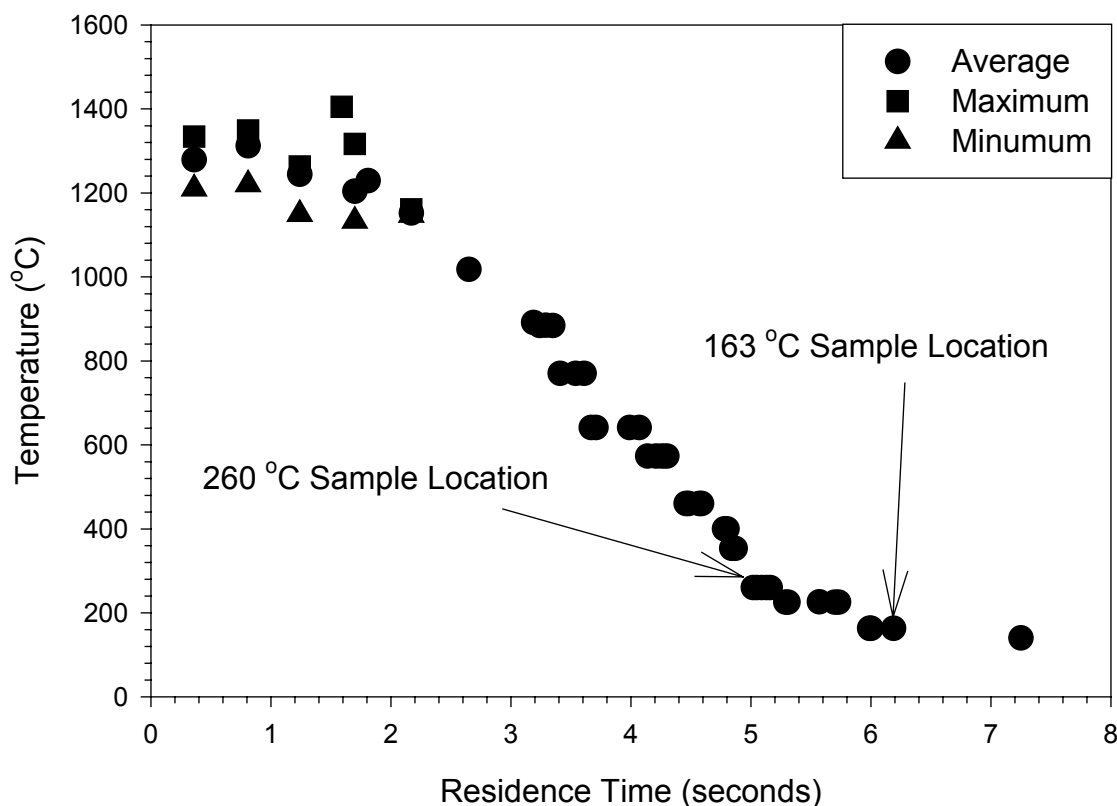


Figure 3. Temperature/time profile of the CRF during the October test with Black Thunder, PRB coal.

Results and Discussion of PRB Speciation Test

Transition from Natural Gas to PRB Coal

Figure 4 shows a graph of the mercury speciation measurements, while firing PRB coal in the CRF, including mercury spikes for validation and data correction. A true zero baseline of mercury was measured on natural gas. The change in mercury measurements during the transition from natural gas to PRB-coal, was sudden and stable. The elemental mercury values increased from zero to $\sim 5 \mu\text{g}/\text{Nm}^3$ (as measured), at both the 163 °C and 260 °C locations. These values remained fairly steady (completely within the limits of the instrument drift) for the next 24 hours. The change in total mercury was similar during this transition from natural gas to PRB-coal. The total mercury numbers increased from zero to $\sim 8 \mu\text{g}/\text{Nm}^3$, for both the 163 °C (325 °F) and 260 °C (500 °F) locations. However, the total mercury numbers continued to increase for the next 3 to 4 hours, finally settling at slightly higher values. Sir Galahad (Hg analyzer within the PS Analytic Monitor) instrument drift affected the data in Figs. 3 and 4. At the end of the PRB-coal firing period (see Figs. 3 and 4), the Sir Galahad mercury monitor was recalibrated (via syringe injection of elemental mercury). Consequently, the mercury numbers were corrected back to $\sim 5 \mu\text{g}/\text{Nm}^3$ (as measured) of elemental mercury and $\sim 8 \mu\text{g}/\text{Nm}^3$ of total mercury, for both sampling locations. The total mercury measurements were slightly higher for PRB coal than that predicted by mass balance, which prediction of Hg^{T} was 6.7 to 7.7 $\mu\text{g}/\text{m}^3$ @6% O_2 in the flue gas. Mercury analysis of solid samples differs significantly, from one laboratory to another. It may be that the amount of mercury in the PRB coal was greater than the values reported by the laboratory. However, the total mercury values for PRB coal in Fig. 4 are probably higher than actual, due to drift of the instrument.

There is a small difference between the elemental mercury trace from the two different sampling locations, which difference decreases somewhat with time. However, this was also true for the total mercury traces. One explanation is that some of the mercury was captured by the high-calcium PRB flyash. This would not be surprising, since hydrated lime has been shown to capture $\sim 33\%$ of the mercury in the flue gas between these two temperature locations, while firing Choctaw America coal [1]. The fact that the difference between the Hg^{T} traces and Hg° traces are similar, indicates that the fraction of mercury oxidized is similar at both locations. Therefore, it does not appear that the fraction of oxidized Hg changed, between the high and low temperature sampling locations. The ratio of total to elemental mercury, before and after the change in absolute mercury measurements, was $\sim 1.63 \pm 0.05$ and $\sim 1.62 \pm 0.05$ respectively.

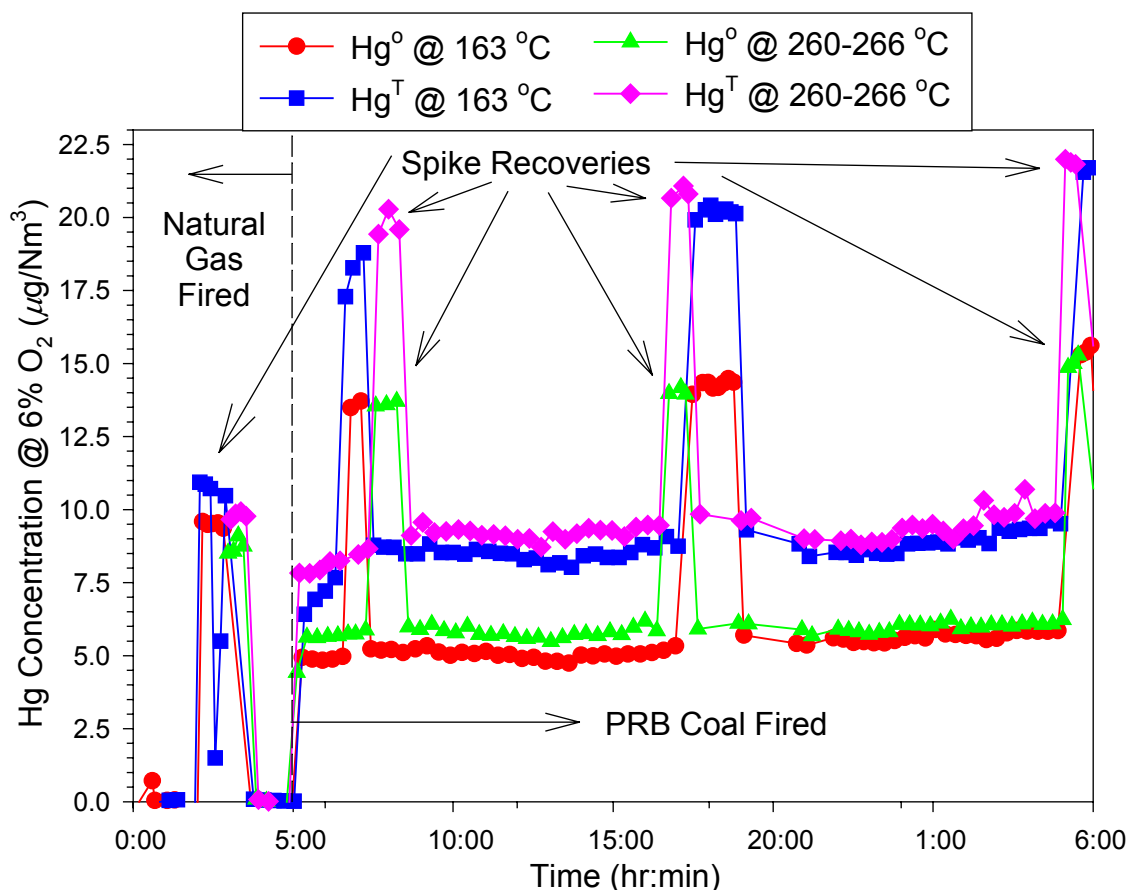


Figure 4. Mercury Speciation data taken with an advanced and customized Hg-speciation semi-continuous monitor, and validated with *spike and recovery* quality assurance.

PRB Speciation

As shown in Fig. 4, the sampling probes were spiked with mercury (~ 9.5 to $9.8 \mu\text{g}/\text{m}^3$) while firing natural gas. The measured recoveries were slightly high when passed through the total-mercury impinger and slightly low when passed through the elemental-mercury impinger. Three spike periods are shown for the PRB-firing period (see Fig.4). The difference in mercury recovery between the stannous chloride and potassium chloride impinger legs was due to differences in impinger chemistry. The KCl impinger captures some of the elemental mercury. In addition, the stannous chloride impinger absorbs some of the CO_2 in the sample stream, thus increasing the concentration of mercury in the sample gas. This inconsistency was examined by spiking behind the sampling probe and at other various locations in the sample train. The spike recoveries were also used to correct for this small artifact in this test.

As mentioned earlier, the Sir Galahad mercury monitor calibration drifted over a day of firing with PRB-coal. The monitor was recalibrated at the end of this period and the data returned to their pre-drift values (or perhaps to slightly below their pre-drift values). From the data shown in Fig. 4, speciation values of mercury in the PRB flue gas were obtained, with fairly small error bars (see Table 4). All data were either taken at or corrected to 6% oxygen in the flue gas. While there is some fluctuation over the 24-hour period of testing, the elemental mercury and total mercury values track each other. Hence, the percentage of oxidized mercury was very

stable. The elemental spike recovery was consistently lower through the elemental mercury leg of the gas conditioning system than through the total mercury leg (see Table 5), and both recoveries were within 10% of the anticipated recovery.

The Hg^{T} -spike recovery was slightly over and the Hg° -spike recovery was slightly under the anticipated recovery. It was considered that the total mercury was less susceptible to false high measurements than the elemental mercury was to false low measurements. It was unlikely that mercury was derived in the sampling system, but it is likely that some mercury was either captured or oxidized by the sampling system. Therefore, the Hg° -values were corrected by multiplying these Hg° -values by the ratio of the Hg^{T} -spike recovery to the Hg° -spike recovery. In this way, the form dependent error in the sampling system was corrected, independent of other errors.

Table 4. Location and Speciation of Hg measurements, while firing PRB coal.

Location	Temperature (°C)	Hg° ($\mu\text{g}/\text{Nm}^3$)	Hg^{T} ($\mu\text{g}/\text{Nm}^3$)	Elemental Fraction %
After Recupatherm 1 (R1 and R2)	260	7.4 +/- 0.93	8.4 +/- 1.1	88.1 +/- 1.5
After Recupatherm 2 (R3 and R4)	163	6.5 +/- 0.44	8.0 +/- 0.70	81.3 +/- 1.0

- An Apogee Scientific QSIS Probe was used to separate the clean-gas sample from the flyash without pulling the gas through a layer of ash.
- The mercury numbers are corrected to 6% oxygen in the flue gas.
- Uncertainties were assigned by applying the information obtained from *spike and recovery*.

Table 5. Spike Recoveries while firing PRB coal.

Sample Type	Temperature (°C)	Spike 1 ($\mu\text{g}/\text{Nm}^3$)	Spike 2 ($\mu\text{g}/\text{Nm}^3$)	Spike 3 ($\mu\text{g}/\text{Nm}^3$)	Average ($\mu\text{g}/\text{Nm}^3$)
Hg°	163	8.30	8.78	8.06	8.38
Hg^{T}	163	10.96	11.13	10.80	10.96
Hg°	260	7.91	8.24	7.81	7.99
Hg^{T}	260	11.59	11.64	11.06	11.43

- The spike injected into the tip of the sampling probe was $\sim 9.7 \mu\text{g}/\text{Nm}^3$.

The uncertainties in the actual elemental and total mercury values presented in Table 4 are somewhat larger than desired, because of uncertainties in the elemental spike delivered. The *spike and recovery system* is continuing to be developed at SRI, and the uncertainty should decrease for future tests. The uncertainty in the fraction of mercury in the elemental form (which was measured directly and not calculated from the other values in the table) is much less however, because this number only depends on the relative amount of mercury oxidized. As shown in Fig. 4, the elemental-mercury concentration directly follows the total-mercury concentration, during the PRB firing period. In fact, the uncertainty in the elemental *fraction* is dominated by changes in the absolute measurements of elemental and total mercury (i.e., the same difference between two small numbers is more significant than between two large numbers), although the difference between the two is steady.

Transition to Choctaw America Coal

Following the Hg-speciation measurements on PRB coal, the transition from firing PRB coal to firing Choctaw America (HvA bituminous) coal was observed. Moisture condensation in the lines (from the gas conditioning system to the Hg-monitor) began to disrupt the data. However, it was shown that no more than five hours were required between coal types, before a new-coal test condition may be examined in the CRF at SRI. For combustion conditions and coal composition see Tables 6 and 7. Table 8 contains the ash composition of the parent coal and ash samples. Choctaw America coal speciation was observed in a previous test as well [1].

Kaolinite Powder Sorbent Test Conditions

Conditions for this test were similar to that of the April 2002 test [1], where hydrated lime was injected into the duct with great success in capturing mercury (33% upstream of the baghouse and ~90% by the baghouse exit). The Choctaw America coal fired had a smaller ash and mercury content than the previous batch of Choctaw coal fired in April. Otherwise, the coals are quite similar (see Table 6 & Ref. 1). Table 7 contains the combustion conditions for this test.

Table 6. Choctaw HvA Bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	2.04	% Carbon	85.39	Hg ($\mu\text{g/g}$)	0.08 – 0.10
% Ash	4.19	% Hydrogen	5.16		
% Volatiles	31.76	% Nitrogen	2.04	Chlorine (%)	0.0127
% Fixed C	62.01	% Sulfur	0.96		
HV (Btu/lb)	14,019	% Oxygen	6.45		

Table 7. Combustion conditions.

Measurement	Range of Value
Overfire Air (OFA) (%)	15.0
Furnace Exit Oxygen (FEO) (%)	3.66 +/- 0.23
Coal Feed Rate (lbs/hr)	260 +/- 2.4
<u>Flue gas composition at sampling point:</u>	
Carbon Dioxide (CO ₂) (%)	13.8 +/- 0.3
Carbon Monoxide (CO) (ppm)	77 +/- 2
Oxides of Nitrogen (NO _x) (ppm)	210 +/- 11
Sulfur Dioxide (SO ₂) (ppm)	522 +/- 4
Oxygen (O ₂) (%)	5.7 +/- 0.13

Table 8. Choctaw HvA Bituminous coal ash analysis.

Parent Coal		Tube Bank		Mass Train	
% Li ₂ O	0.06	% Li ₂ O	0.05	% Li ₂ O	0.04
% Na ₂ O	1.1	% Na ₂ O	1.0	% Na ₂ O	1.4
% K ₂ O	2.0	% K ₂ O	1.5	% K ₂ O	1.7
% MgO	1.1	% MgO	1.8	% MgO	2.4
% CaO	2.5	% CaO	6.8	% CaO	10.4
% Fe ₂ O ₃	13.8	% Fe ₂ O ₃	11.9	% Fe ₂ O ₃	11.3
% Al ₂ O ₃	31.4	% Al ₂ O ₃	27.8	% Al ₂ O ₃	29.3
% SiO ₂	42.6	% SiO ₂	43.5	% SiO ₂	39.5
% TiO ₂	1.3	% TiO ₂	1.8	% TiO ₂	1.8
% P ₂ O ₅	0.16	% P ₂ O ₅	0.26	% P ₂ O ₅	0.40
% SO ₃	2.8	% SO ₃	2.5	% SO ₃	0.90
% LOI	---	% LOI	0.27	% LOI	4.2
% UBC	---	% UBC	0.10	% UBC	3.51

Results and Discussion of Kaolinite Test

Kaolinite has a clay structure, unique for its ability to capture metals and metal oxides at high temperatures. Upon injection of powdered kaolinite into high-temperature flue gas, it flash calcines to form meta-kaolinite, possessing meso-pore gaps between stacked layers of alternating and highly-ordered alumina/silica layered platelets. The octahedral positions of the alumina surface are only 2/3 filled with aluminum atoms in the kaolinite crystal. However, aluminum is tetrahedrally coordinated in meta-kaolinite, the reactive crystal structure. In this state, the alumina layer is well disposed to accommodate metals into the interstitial sites within its matrix, which then reverts back to a stable octahedral coordination, where the captured metal is trapped in a stable compound. Kaolinite has been shown to be effective at capturing lead, cadmium, and sodium [2], which are all semi-volatile metals.

In the tests performed this quarter, kaolinite was injected at several different temperature locations (from 600 °C (1100 °F) to 1150 °C (2100 °F)) in the CRF, while firing Choctaw America coal. Mercury removal was measured well downstream, ahead of and behind the baghouse. Hence, the ability of the sorbent to remove mercury anywhere in the flue gas train was examined, from high to low temperatures. Sorbent concentration was also varied from low to a loading half that of the flyash loading. Kaolinite sorbent was completely *ineffective* at capturing mercury from the flue gas at either high or low temperatures.

Chlorine Test Conditions

Chlorine Speciation

Figure 5 contains thermodynamic predictions of chlorine speciation in the CRF while firing PRB coal. These thermodynamic predictions (and those shown in Fig. 6) were made using CEA, a multi-component chemical equilibrium code [3] using measured PRB flue gas composition as input. As shown, the dominant driving force at the burner and well downstream is toward the formation of HCl. However, a smaller but significant driving force exists at the burner and overfire air to yield some fraction of the chlorine as radicals. Hence, rapid quench could prevent the time necessary to destroy these radicals and present a significant concentration

of these radicals to react with Hg° at lower temperatures. This has been discussed in the literature [4, 5].

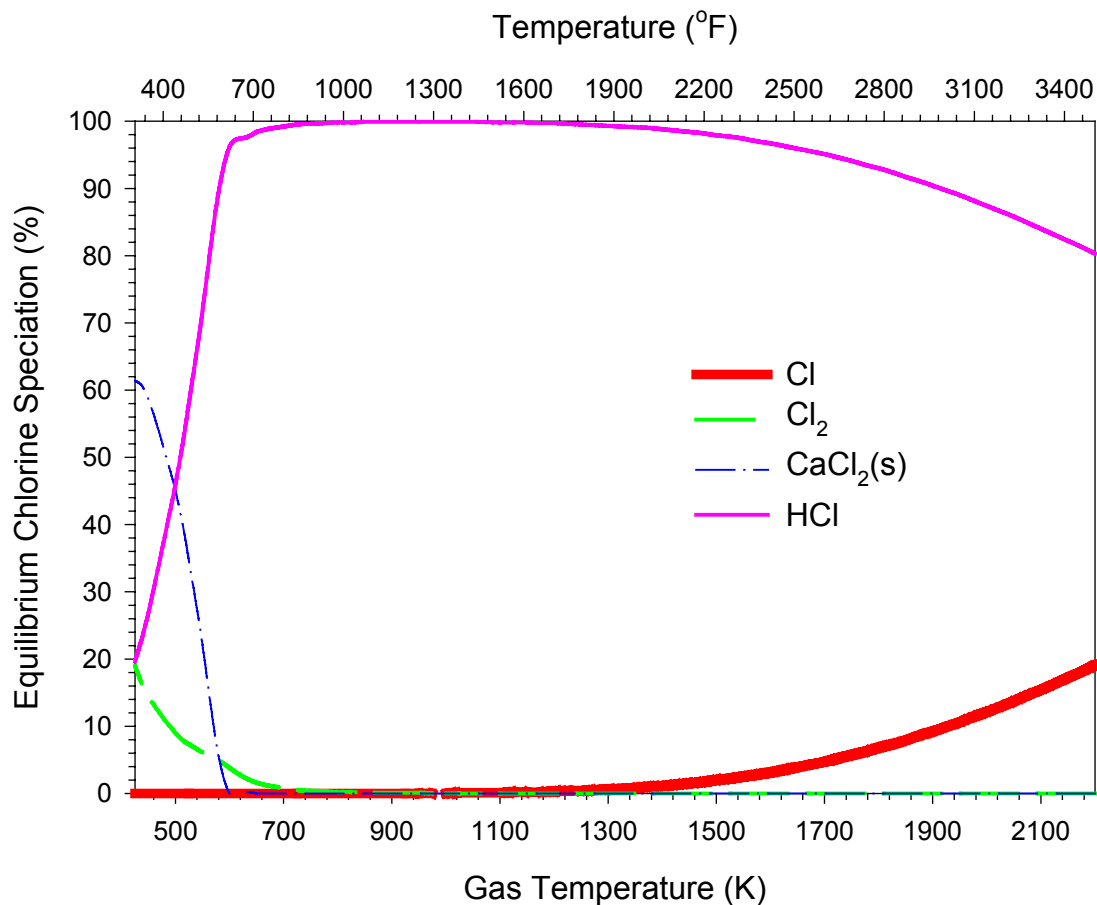


Figure 5. Chlorine speciation in the CRF, while burning PRB, as predicted by CEA-thermochemical equilibrium [3].

Chlorine gas (Cl_2) is not thermodynamically promoted at high temperatures. However, below 370°C (644 K or 700°F) a significant driving force toward the formation of Cl_2 develops, a driving force which begins to dominate over the formation of HCl below 260°C (533 K or 500°F). Given that chlorine speciation is kinetically controlled in coal-fired boilers, several observations can be made from the thermodynamic predictions in Fig. 5. It is likely that chlorine gas injection through the burner will be entirely converted to HCl and Cl^- in the furnace. Apparently, any form of chlorine injected through the primary-air line will be converted in the furnace to HCl and a smaller amount of Cl^- . The result down stream ($\sim 600^\circ\text{F}$) will be to increase the total amount of chlorine in the flue gas by the amount injected through the burner. The form of chlorine will be primarily HCl . However, as more total chlorine is injected through the burner, a small but higher concentration of Cl^- may be present downstream. Although a driving force toward the formation of Cl_2 begins to form below 370°C (644 K or 700°F), the form of chlorine is expected to be dominated by kinetics at this point. Thus, the majority of the HCl is expected to remain in that form for the residence times that exist in full-scale power plants. Furthermore, if Cl_2 gas was injected at a lower temperature location downstream where

the thermodynamic driving force is more favorable to its formation, then it would likely remain in the form in which it was injected.

Mercury Speciation

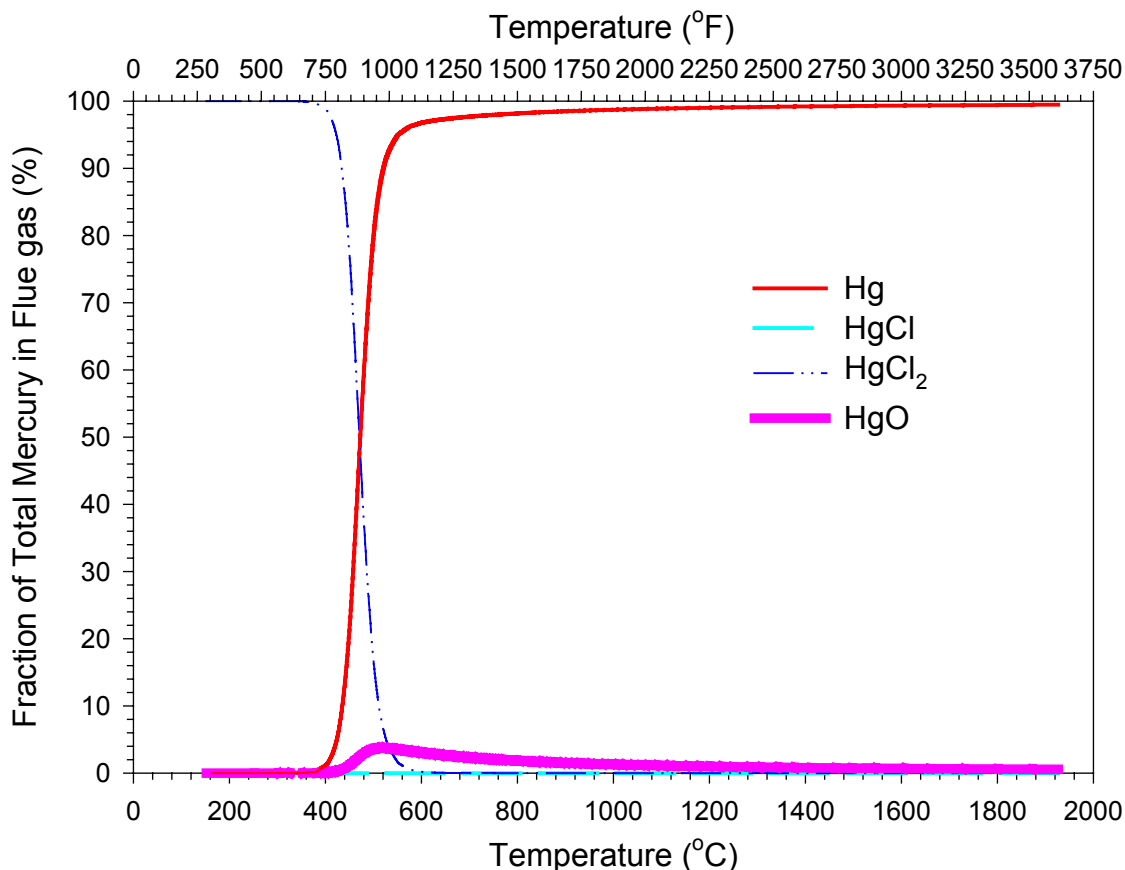


Figure 6. Mercury speciation in the CRF, while burning PRB, as predicted by CEA-thermochemical equilibrium [3].

Figure 6 illustrates the thermodynamic predictions of Hg-speciation in the CRF, while firing PRB-coal. Consistent with the literature [4, 5], all of the mercury entering the furnace with the coal is predicted in the elemental form. This thermodynamic driving force does not begin to change significantly until below ~ 1100 °F. At this point, we know that Hg-speciation is controlled by kinetics [4-8], given the temperature/time history of the CRF and full-scale boilers. The driving force however, quickly (by ~ 800 °F, see Fig. 6) favors the formation of HgCl₂ only. Hence, in order to promote the complete oxidation of mercury, it is only necessary to lengthen the residence time and/or increase the kinetic rate. This can be accomplished by increasing the homogeneous reaction rate (altering the concentration of gas phase reactants) or by increasing the heterogeneous rate (i.e., catalytic enhancement – UBC, iron oxide, etc.). The heterogeneous reaction rate depends on numerous interrelated mechanisms for both chlorine speciation and in-turn Hg-speciation, some of which have been discussed in the literature [4-10].

PRB Coal and Ash Analysis and Combustion Conditions

Tables 9-12 contain the PRB coal analysis, combustion conditions, flue-gas composition, and the condition-dependent ash analysis, from the chlorine injection tests.

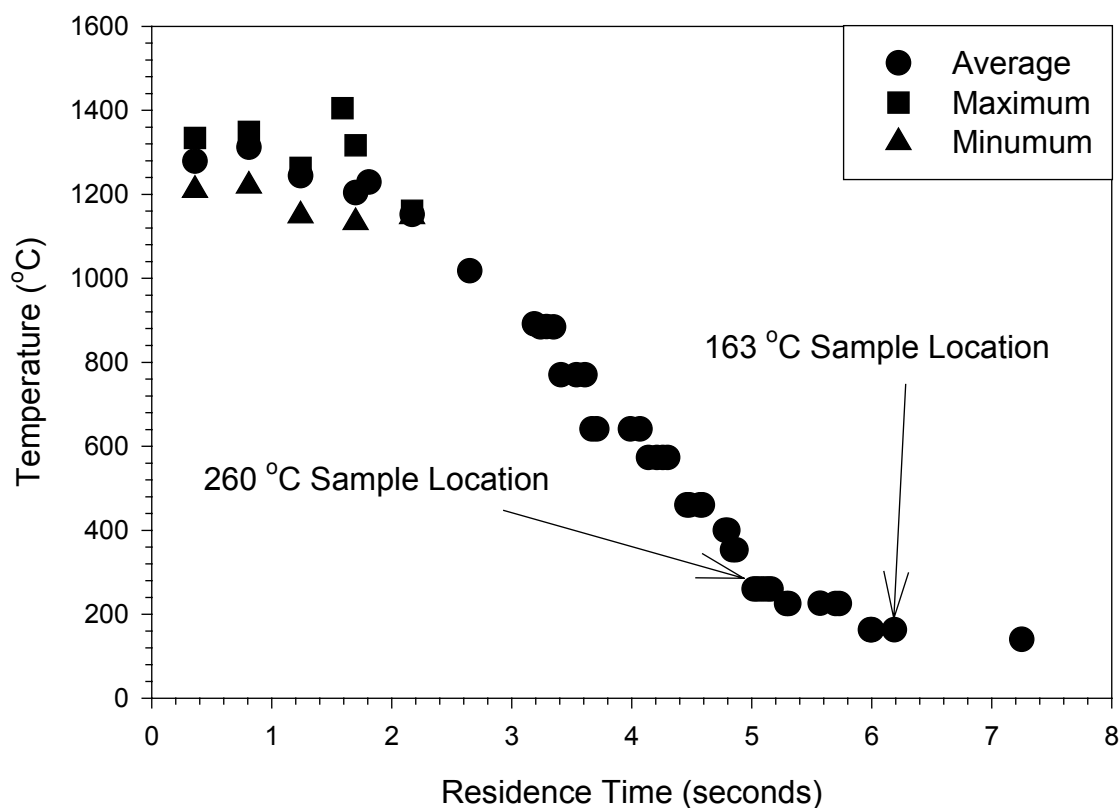


Figure 7. Temperature/time profile of the CRF during the October 2002 test with Black Thunder, PRB coal.

Table 9. PRB sub-bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	14.00	% Carbon	74.55	Hg ($\mu\text{g/g}$)	0.07 – 0.08
% Ash	5.92	% Hydrogen	4.78		
% Volatiles	37.57	% Nitrogen	1.03	Chlorine (%)	0.0130
% Fixed C	42.70	% Sulfur	0.37		
HV (Btu/lb)	9,969	% Oxygen	19.27		

A temperature/time profile specifically for the PRB coal-fired conditions of this test is presented in Figure 7. Vapor phase mercury concentrations were measured at the two flue-gas temperatures noted in the figure. Manual measurements of HCl concentrations and particulate mass, chloride, and mercury concentrations were measured at flue-gas temperatures of approximately 163 °C (325 °F). This flue-gas temperature (325 °F) was also the sample point in the CRF for the CEM monitors (O_2 , CO_2 , CO , NO_x , SO_2).

Table 10. Combustion conditions for baseline (NO Chlorine Injection).

Measurement	Range of Value
Overfire Air (OFA) (%)	15.0
Furnace Exit Oxygen (FEO) (%)	3.87 +/- 0.21
Coal Feed Rate (lbs/hr)	365 +/- 2.5
<u>Flue gas composition at sampling points:</u>	
Carbon Dioxide (CO ₂) (%)	14.0 +/- 0.2
Carbon Monoxide (CO) (ppm)	67 +/- 2
Oxides of Nitrogen (NO _x) (ppm)	159 +/- 11
Sulfur Dioxide (SO ₂) (ppm)	198 +/- 8
Oxygen (O ₂) (%)	6.2 +/- 0.1

Table 11. Baseline PRB sub-bituminous coal ash analysis.

	Parent Coal	Tube Bank	Mass Train
% Li ₂ O	0.01	0.01	0.02
% Na ₂ O	1.4	1.1	2.4
% K ₂ O	0.50	1.4	0.67
% MgO	4.3	3.4	4.9
% CaO	22.0	19.5	26.2
% Fe ₂ O ₃	6.0	8.0	8.2
% Al ₂ O ₃	15.4	17.2	19.1
% SiO ₂	35.4	41.0	30.5
% TiO ₂	1.3	1.8	1.9
% P ₂ O ₅	0.70	0.41	1.2
% SO ₃	11.5	4.9	3.7
% LOI	---	0.05	0.23
% UBC	---	0.04 +/- 0.01	0.07 +/- 0.01

Table 12. Mass Train Ash Analysis as a Function of Flue Gas Chlorine Content.

Species	^a 133 ppm Cl ₂	^b 69 ppm Cl ₂	^b 17 ppm Cl ₂	^b 9 ppm Cl ₂	^c Baseline Coal
% Li ₂ O	0.02	0.02	0.01	0.01	0.02
% Na ₂ O	1.3	1.9	1.9	1.9	2.4
% K ₂ O	0.48	0.59	1.2	1.2	0.67
% MgO	5.4	5.2	5.2	5.3	4.9
% CaO	28.2	26.1	26.1	27.0	26.2
% Fe ₂ O ₃	7.3	7.4	7.3	7.4	8.2
% Al ₂ O ₃	19.1	19.0	18.9	18.2	19.1
% SiO ₂	31.8	32.6	32.3	33.0	30.5
% TiO ₂	2.0	1.8	2.1	2.0	1.9
% P ₂ O ₅	1.1	1.1	1.0	1.0	1.2
% SO ₃	2.1	3.1	2.8	2.7	3.7
% LOI	0.72	0.23	0.24	0.21	0.23
% UBC	0.09 +/- 0.01	0.06 +/- 0.01	0.05 +/- 0.01	0.06 +/- 0.02	0.07 +/- 0.01
Chloride(μg/g)	7306	< 0.01	< 0.01	< 0.01	< 0.01
Hg (μg/g)	0.537+/-0.011	0.086+/-0.011	0.083+/-0.004	0.069+/-0.006	0.067+/-0.016

a. Chlorine was added with the primary burner air in this case.

- b. Chlorine gas was injected just before the air heater (1064 °F) for these tests.
- c. The chlorine flue gas content was 0.6 ppm at the sampling location.

Results and Discussion of Chlorine Injection Tests

Chlorine Injection Recoveries

Data was recovered from five conditions, relative to chlorine injection. Four conditions involved Cl₂-gas injection to increase the flue gas Cl₂ concentration to 9, 17, 69, and 133 ppmv, respectively. In addition to these four chlorine injection conditions, a baseline condition was examined, which possessed only the chlorine in the flue gas that entered with the coal.

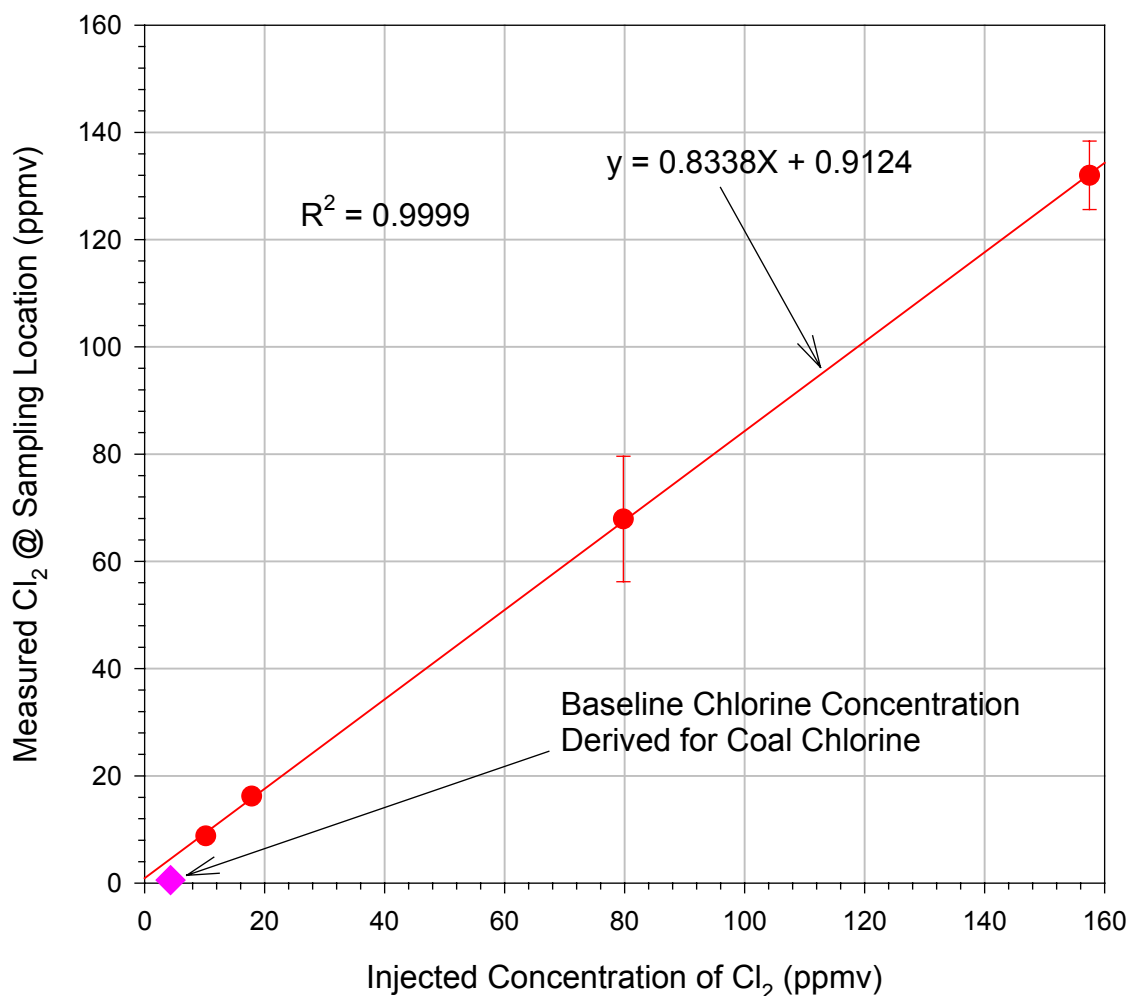


Figure 8. Measured in-furnace chlorine (Cl₂) concentrations compared with attempted injection concentrations.

Figure 8 compares the recoveries of chlorine from manual gas measurements in the duct downstream of the mercury monitor sampling location with the calibrated injection amounts. The linearity of the graph illustrates (1) the good precision of the chlorine injection system (although the calibration itself was somewhat off), (2) the excellent precision of the gas-phase chlorine measurements (the measured values were accepted as the actual flue gas

concentrations), and (3) that NO significant amount of chlorine was lost within the CRF, either to the walls or ash. It is also interesting to note that the mass balance of coal chlorine showed low recovery for the baseline. Apparently, the coal-bound chlorine was more susceptible to adhere to the ash than was the injected chlorine. Perhaps much of the coal-bound chlorine was not devolatilized in the furnace.

Effect of Chlorine on Unburned Carbon

Figures 9 and 10 illustrate the effect of chlorine injection on unburned carbon (UBC), while firing PRB coal in the CRF. Figure 9 indicates that the scatter in the UBC numbers is inconsistent. More importantly, Fig. 10 illustrates that all of the UBC numbers are very low compared to the average UBC numbers for a bituminous coal burned in the CRF. It has been suggested that UBC may have a significant effect on mercury speciation, by catalyzing the regeneration of chlorine radicals [9], according to the following equation:



However, considering the low and fairly consistent UBC values of the PRB ash, it is likely that the impact of UBC was a secondary effect at best, during this investigation.

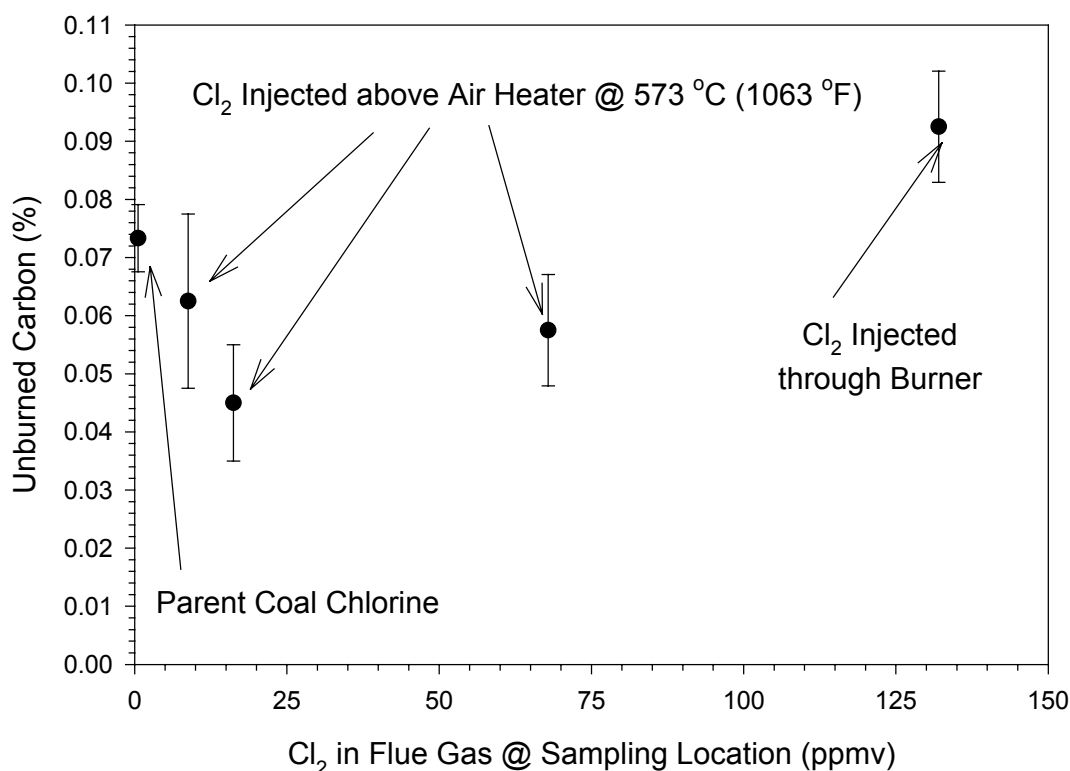


Figure 9. Effect of chlorine gas (Cl₂) injection on unburned carbon in PRB flyash.

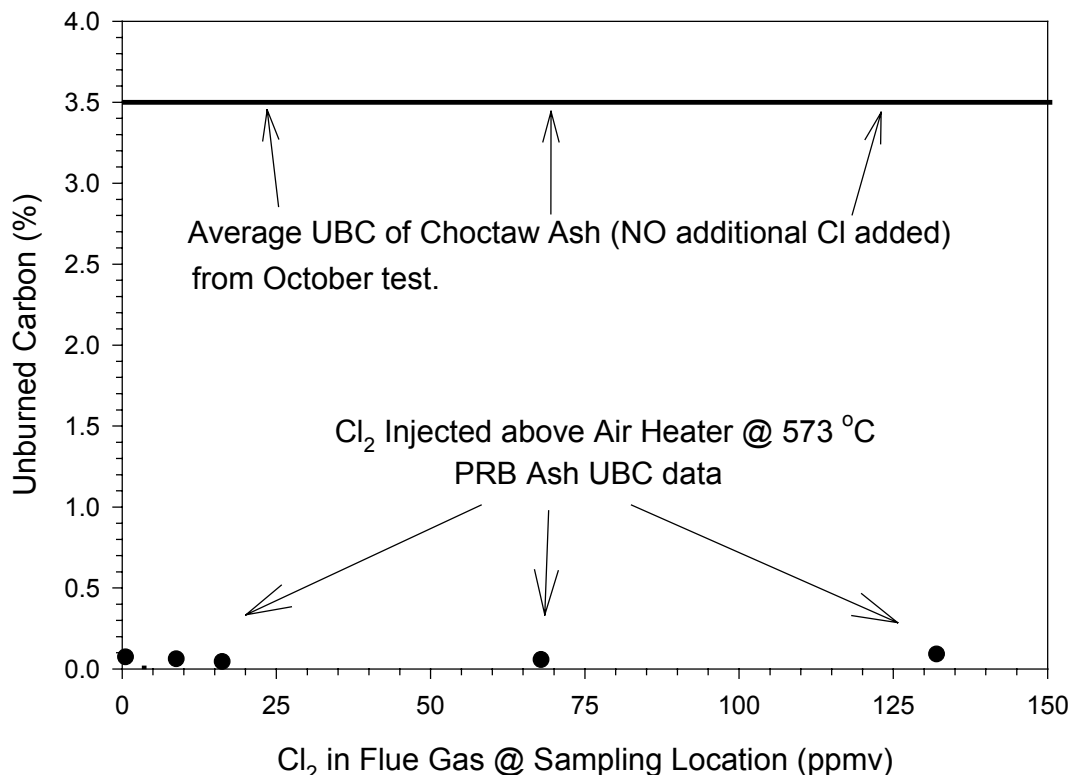


Figure 10. UBC in PRB flyash samples (taken during this test) compared with typical Choctaw America ash samples, produced under the same conditions.

Effect of Chlorine on Flue-Gas Composition

As shown in Fig. 11, the presence of chlorine in the flue gas had little effect on the flue-gas composition of NO_x, CO, CO₂, or O₂. The NO_x data are a little erratic, due to drift in the calibration of the instrument, but were unaffected by chlorine injection. The sulfur dioxide concentration detected by the monitor, however, was significantly altered by chlorine gas injection, as shown in Fig. 12. The measured decrease in SO₂ was directly proportional to the concentration of Cl₂ gas injected (see Fig. 12) above the air heater. However, when a high-concentration of Cl₂ was injected through the burner, the effect on SO₂ was much less significant. As illustrated in Fig. 5, the chlorine injected through the burner was primarily in the form of HCl, even once it reached lower flue-gas temperatures, while the Cl₂ injected above the air pre-heater tended to stay in that form. Consequently, the effect on detected SO₂ is clearly associated with Cl₂ gas and not HCl. Furthermore, the recovery of chlorine in gas-phase sampling was high (see Fig. 8) for all chlorine injection conditions. In addition, a qualitative observation of the sulfite and sulfate peaks from the chromatograph of the impinger solutions, indicated high sulfur recoveries. Therefore, there was no loss of chlorine to the particulate during Cl₂ injection, and it is likely that little loss of sulfur to the particulate occurred, at least before the sampling ports.

Chlorine gas is not an interference to the SO₂ monitor, which uses UV light at the wavelength absorbed by SO₂. SO₂Cl₂ is thermodynamically favored through the reaction of SO₂ with Cl₂ at temperatures below 150 °C, and its formation can be rapid at lower temperatures.

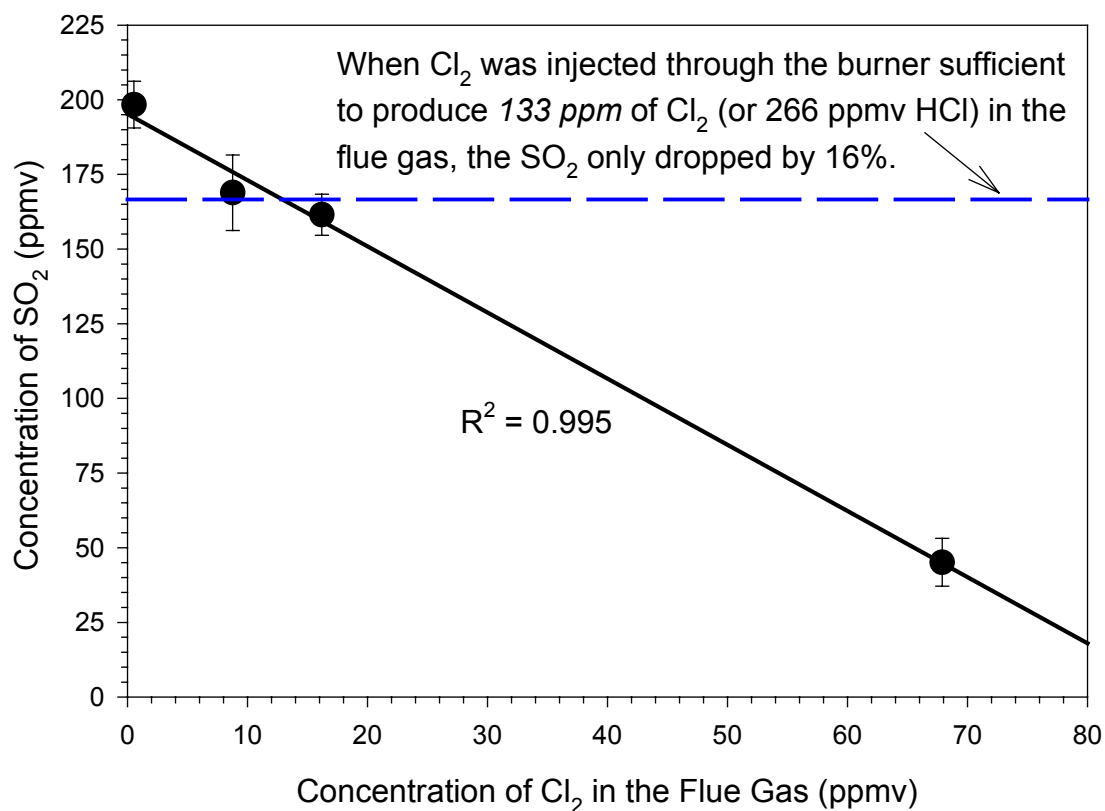


Figure 11. Effect of chlorine on flue gas composition.

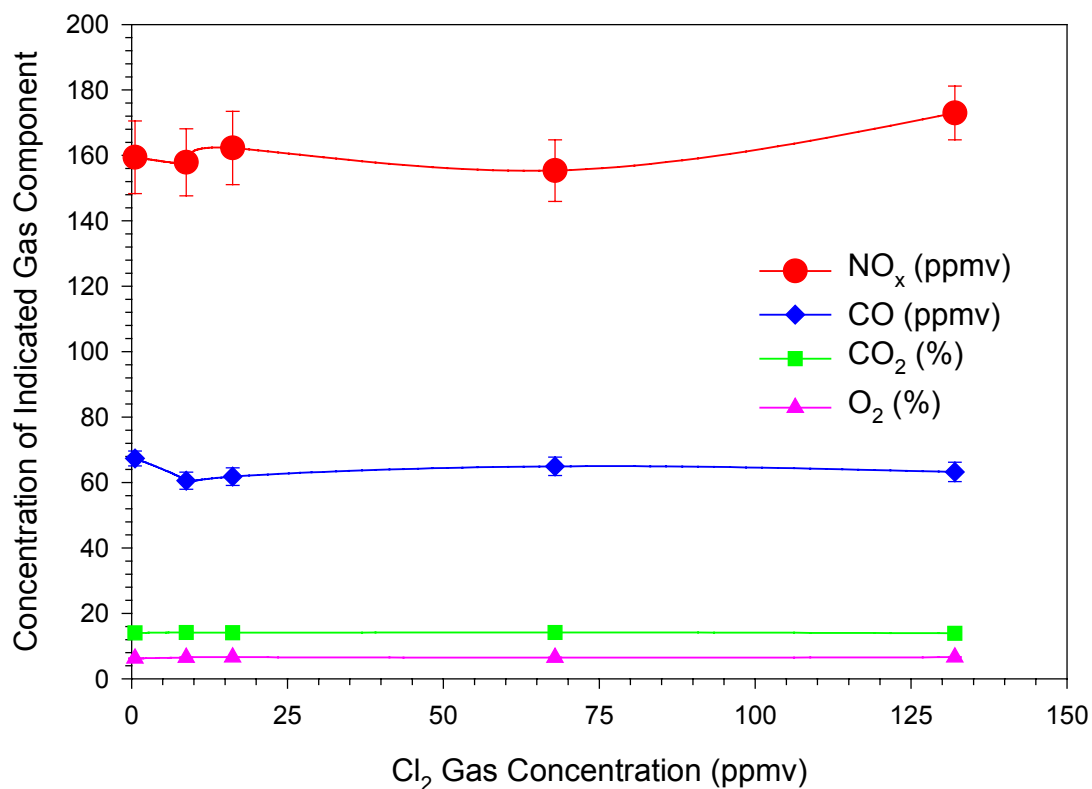


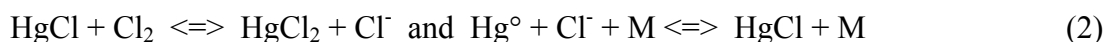
Figure 12. Impact of Cl_2 gas injection on SO_2 Measurements.

Hence, the flue-gas concentration of SO₂ was not altered by the presence of Cl₂, but SO₂Cl₂ formed in the cooling gas stream in the moisture condenser ahead of the SO₂ analyzer, thus lowering the concentration of SO₂ detected. Figure 12 thus shows an artifact of the flue-gas conditioning system ahead of the SO₂ analyzer.

Effect of Cl₂ Injection on Hg-Speciation

Interference of chlorine with the gas conditioning system in the mercury monitor and other difficulties with the PSA monitor resulted in large uncertainties in the Hg-speciation measurements. For example, chlorine gas that passed through the KCl impinger *poisoned* the gold trap in the Sir Galahad Hg monitor, yielding low elemental mercury measurements. Corrections were made based on the *recoveries of the spikes*, but the validity of these corrections is currently uncertain. In addition, only the data from the 260 °C (500 °F) sampling location was obtained. In spite of the high uncertainty in the data, a general *qualitative correlation* between the flue-gas chlorine concentration and the fraction of mercury oxidized appears to exist. Catalytic properties of the high-calcium PRB ash are not favorable to promoting mercury oxidation (i.e., low UBC and observed to produce low Hg oxidation in ICR data [11]). Therefore, it is likely that homogeneous mechanisms can completely account for any increase in Hg oxidation caused by chlorine injection, under the conditions tested.

The following equations represent alternative homogeneous pathways (examples, not a comprehensive list) whereby the two different chlorine forms (HCl and Cl₂) may promote mercury oxidation [4-8], as follows:



It is true that some Cl₂ gas may have persisted downstream, when the Cl₂ was injected through the burner. Alternatively, some HCl may have been converted to Cl₂. Evidence of this is in the fact that the Cl₂ injected through the burner decreased the detected SO₂ concentration by 16%, which decrease apparently occurred through a gas-phase reaction of Cl₂ with SO₂ (see above). However, a decrease in the detected SO₂ of 16% would have been associated with a small amount of Cl₂ (~20 ppm), determined by comparing to the effect of injecting Cl₂ above the air heater (see Fig. 12). Unfortunately, chlorine injection interferences with the sampling system and perhaps a valve-switching interference made it impossible to quantify the extent of mercury oxidation, especially when chlorine was injected through the burner. However, a significant increase in mercury oxidation was observed in the monitoring measurements during chlorine injection through the burner, at least some of which may have occurred in the sampling system.

Effect of Chlorine Injection on Hg Capture by Flyash

Table 13 illustrates the effect of chlorine injection on mercury capture by the high-calcium PRB flyash. Regardless of the amount of Cl₂-gas injected (above the air pre-heater), chlorine was ineffective at increasing mercury uptake by the ash. However, when chlorine was injected through the burner, the uptake by the ash was greater than 30% of the total mercury (based on a mass balance). This phenomenon is unrelated to differences in the extent of mercury oxidation, since significant oxidation occurred for all chlorine injection conditions. The removal

of mercury by the PRB ash was associated with ash conditioning caused by the increase in HCl when chlorine was injected through the burner, which HCl was not present when Cl₂ was injected above the air pre-heater.

Table 13. PRB Flyash Hg-Uptake Enhancement by Hydrochloric Acid (HCl)

Isokinetic Ash Samples	Concentration and Form of Chlorine in the Flue Gas (ppm)				
	^a 0.6 Cl ₂	9 Cl ₂	17 Cl ₂	69 Cl ₂	133 (2HCl)
Chloride in Ash (μg/g)	< 0.01	< 0.01	< 0.01	< 0.01	7306
Mercury in Ash (μg/Kg)	67	69	83	86	537
%HgCl ₂ in Flue Gas @ 200 °C	< 20%	< 40%	> 50%	> 50%	> 50%
Hg-Removal From Flue gas (%)	< 5%	< 5%	< 5%	< 5%	> 30%

a. This represents the baseline condition, when no chlorine was injected into the facility.

Table 13 contains, among other things, the concentration of chloride measured in the mass train samples, taken during the different chlorine injection conditions. The concentration of chloride in the ash taken while injecting Cl₂ through the burner is many orders of magnitude greater than that in ash taken when Cl₂ was injected above the air pre-heater. The HCl formed in the furnace when injecting Cl₂ gas through the burner, conditioned the ash so that it would effectively scavenge the mercury (presumably HgCl₂). Based on a mass balance, this accounts for less than five percent of the chlorine injected into the furnace. However, it provided sufficient conditioning to capture greater than 30% of the mercury from the flue gas by the time it reached the two mass-train sampling locations, just downstream of the mercury monitor. These two sampling locations are about 10 and 20 feet ahead of the baghouse, respectively. It is not known from the data obtained in this work whether all of the mercury was captured before the mass train location or whether mercury was also captured by the ash on the mass-train filters. Further experiments are needed to determine if this ash conditioning effect continues to enhance capture by the ash in the baghouse.

The data in Table 13 indicate that PRB ash may be converted into an effective mercury chemi-sorbent by conditioning with a small amount of HCl, and sufficient chlorine and/or catalyst injection to promote the complete oxidation of all of the mercury in the flue gas. This concept may have many practical applications, including ash conditioning upstream of an ESP to capture all of the mercury on PRB ash without building new capital equipment.

Figure 13 illustrates the total mercury values obtained from the semi-continuous mercury monitor during injection of Cl₂ through the burner. During the measurement, the monitor cycled through four channels, including the two different-sampling-temperature elemental-mercury channels.

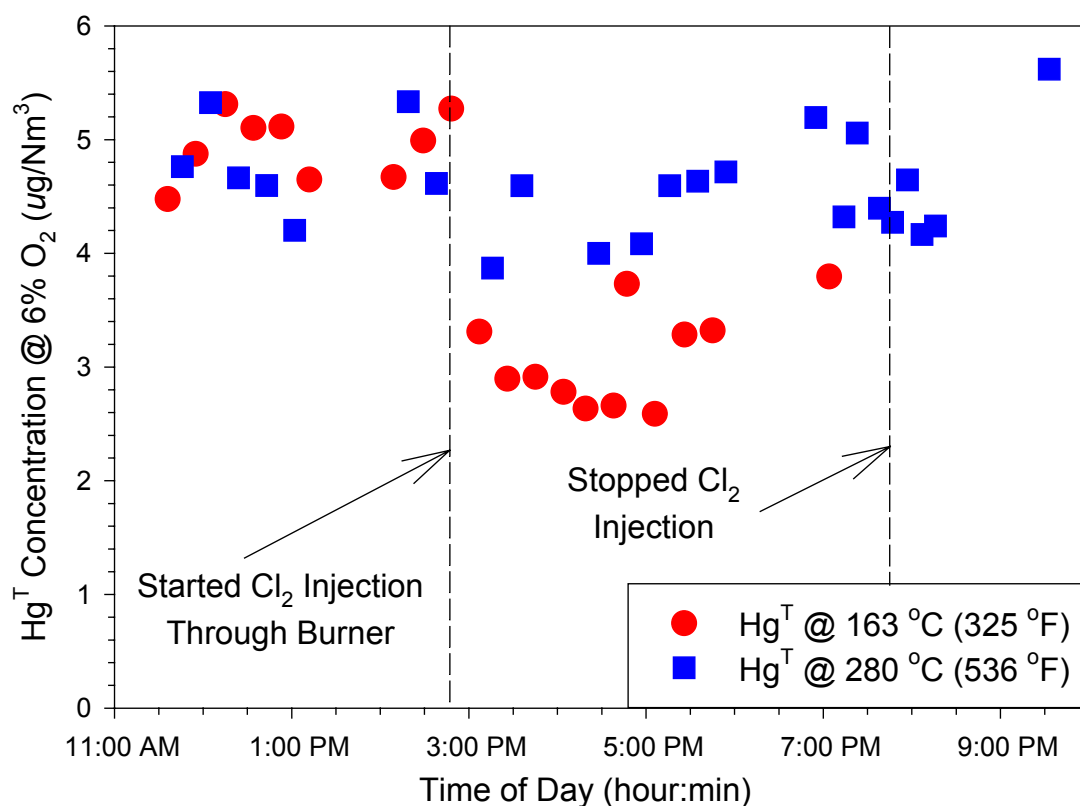


Figure 13. Total mercury data from the PS Analytical Monitor, with 133 ppmv of Cl₂ (266 ppmv HCl) in the flue gas, injected through the burner.

Interference was later observed between the different channels, as the monitor automatically switched from one channel to another. Specifically, the measurement of a stream with a low concentration of mercury would cause the next channel to read lower than its actual mercury concentration. Similarly, the measurement of a stream with a high concentration of mercury would cause the next channel to read higher than its actual mercury concentration. This interference was dealt with later in the run week, when Cl₂ gas was injected above the air pre-heater. However, the data in Fig. 10 was adversely affected by interferences associated with stream selector switching between the low-Hg^o streams and the higher-Hg^T streams. Nevertheless, some valuable qualitative information was gleaned from the data presented.

The total mercury values for the 260 °C (500 °F) sampling condition (see Fig. 13) did not decrease when chlorine injection was started. Since this was the stream with the highest concentration of mercury, any interference would tend to reduce the measured concentration. Therefore, this is evidence that *NO* mercury was captured on the ash above the 260 °C (500 °F) location. However, the total mercury measurement for the 163 °C (325 °F) location dropped sharply when the Cl₂ injection began. These data were also affected by the interference of channel switching (and other associated problems not discussed in detail in this report). Therefore, quantitative data may not be extracted from these measurements. However, the sharp decrease in total mercury at the 163 °C (325 °F) location, indicates that a significant fraction of the total mercury was removed by the flyash prior to the 163 °C (325 °F) sampling location. In addition, a mass balance on the mass-train ash samples, taken just downstream of the 163 °C

(325 °F) location, revealed that >30% of the mercury in the flue gas was removed by the flyash (disperse phase + removal by the ash filter-cake) during the period of chlorine injection through the burner (see Table 4 and Fig. 10).

It is not possible to determine from the mass-train data whether or not additional mercury was removed from the flue gas after sampling. Flue-gas was pulled through the mass-train filter.

Conclusion

It has been shown that *spike and recovery* is a very useful tool and absolutely necessary in order to obtain the *accurate and precise data required* to investigate mercury speciation in coal-fired flue gas.

Mercury speciation characteristic of PRB sub-bituminous coal has been reproduced in the CRF, indicating that mercury speciation within the CRF is representative of full-scale boilers, to the extent that accurate data exists for full-scale units [11]. Specifically, the elemental mercury yield while firing PRB coal was >80%. While firing Choctaw coal, the elemental mercury yield was only ~40% [1]. Of course, the comparison for HvA bituminous coal (like Choctaw America) is limited by the uncertainty in the data obtained in the CRF (no spike and recovery was available for the previous test), as well as the uncertainty in the ICR database [11].

The difference in speciation yield between the PRB sub-bituminous and Choctaw HvA bituminous coal-fired tests is especially interesting, because both coals had low chlorine content. Thus, the dominating mechanisms were likely more affected by other parameters such as: SO₂ and NO_x concentrations and fly ash composition (i.e., iron, calcium, UBC).

By employing careful experimentation and implementing *spike and recovery* with mercury monitoring, SRI was able to obtain a very good set of data for Black Thunder PRB coal. This set of data is a beginning to the *excellent quality data necessary* for the success of this program.

Based on the success and learning experiences of this test, further development of the *spike and recovery* system has been accomplished and is currently being tested. In addition, impinger chemistry investigations will be performed along with an investigation of possible sampling system impacts on mercury speciation. The final development of the *spike and recovery* system will require an oxidized-mercury spike in addition to the current elemental-mercury spike.

It was found that kaolinite powder sorbent, though effective for high-temperature capture of semi-volatile metals (Pb, Cd, Na), was ineffective at capturing mercury at either high or low temperatures.

Some time was spent this quarter preparing for the new tasks identified following the ARCADIS benchscale results performed this summer. In addition, many analytical problems were encountered during the tests with the semi-continuous Hg monitor, which prevented the execution of the intended experiments. However, important findings were extracted from the available data. An increasing relationship between Cl₂ concentration in the flue gas and mercury oxidation was observed. It was also shown that HCl, produced by injecting Cl₂ through the burner, conditioned the ash downstream, making it effective at removing some oxidized mercury at temperatures relevant to full-scale air heaters. The effect of chlorine gas on mercury removal was tested, by moving the injection location to a lower temperature, just above the air pre-heater, which allowed the Cl₂ to persist in the flue gas. Chlorine gas (Cl₂) was ineffective at conditioning the ash for mercury sorption, even though it was effective at oxidizing the elemental mercury to form HgCl₂.

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